

# Cleaning of niobium surface by plasma of diffuse discharge at atmospheric pressure

V F Tarasenko<sup>1,2</sup>, M V Erofeev<sup>1,2</sup>, M A Shulepov<sup>1</sup> and V S Ripenko<sup>1</sup>

<sup>1</sup> Institute of High Current Electrons, 2/3 Akademicheskoy ave., Tomsk, 634055, Russia

<sup>2</sup> National Research Tomsk Polytechnic University, 30 Lenin ave., Tomsk, 634050, Russia

E-mail: VFT@loi.hcei.tsc.ru

**Abstract.** Elements composition of niobium surface before and after plasma treatment by runaway electron preionized diffuse discharge was investigated in atmospheric pressure nitrogen flow by means of an Auger electron spectroscopy. Surface characterizations obtained from Auger spectra show that plasma treatment by diffuse discharge after exposure of 120000 pulses provides ultrafine surface cleaning from carbon contamination. Moreover, the surface free energy of the treated specimens increased up to 3 times, that improve its adhesion property.

## 1. Introduction

Nowadays surface modification of metals and dielectrics by low-temperature plasma formed in different types of gas discharge are widely used in microelectronics, nano-technology and medicine. A number of methods have been developed for the surface modification using low-pressure gas discharge, such as plasma nitriding [1], plasma spraying [2], treatment by low energy high current electron-beam [3]. However, most of these plasma sources require special vacuum equipment, which limits integration in production lines and increasing its cost. In this work, runaway electron beam and X-rays formed in non-uniform electric field by applying high voltage pulses of nanosecond duration to the electrode with small radius of curvature was used to generate a diffuse discharge in a working gas of atmospheric pressure [4]. In this type of discharge called a runaway electrons preionized diffuse discharge (REP DD), the plane ground electrode experiences action of dense plasma, a shock wave, a super short avalanche electron beam, as well as optical radiation of different spectral regions, including UV, VUV, X-rays from the discharge plasma. Voltage pulse polarity, and consequently direction of ions and electrons motion, define type of the treatment on the ground electrode. Thus the use of REP DD, which can generate volume non-thermal plasma at atmospheric pressure, provides scientists another approach for surface modification with low cost, simple facilities and easy operation.

In our previous work [5], pulsed generator RADAN-220 was used for diffuse discharge formation. The main disadvantage of this generator is a low repetition pulse rate – less than 1 Hz, that demands of long exposure time to obtain any significant results of discharge plasma treatment. In this work, the experimental setup based on GIN-100 generator with pulse repetition frequency up to 1000 Hz was developed, that allows to shorten the exposure time for plasma treatment. The aim of the work was to study the effect of diffuse discharge plasma formed in nitrogen flow of atmospheric pressure on the surface of niobium. Due to the use of niobium in modern high-technological equipment, e.g., SQUID magnetometer in nuclear magnetic tomographs, high-frequency cell in elementary particle accelerators and superconducting solenoids, cleanness of Nb surface and thin Nb-films from oxides or other contaminants is very important.



## 2. Experimental setup and methods of measurements

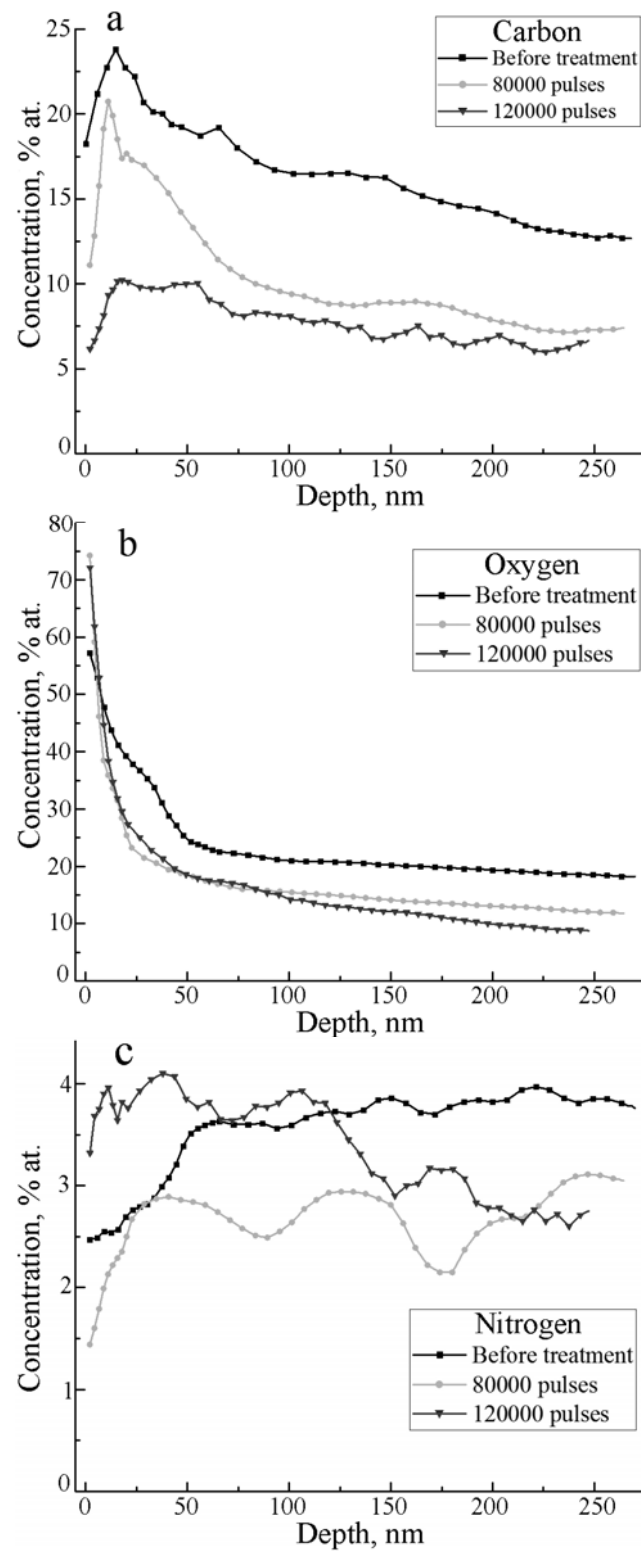
Design of the discharge chamber has been reported in [6]. In the experiments, a REP DD was formed by applying negative voltage pulses from GIN-100-1 generator (Antares Ltd., Russia) with a FWHM of 4 ns with amplitude up to 80 kV to electrode of small curvature radius at a pulse repetition frequency of up to 100 Hz. Typical waveforms of voltage pulses at the discharge gap consists of a sequence of voltage pulses of both polarities, so plane electrode is affected by action of electron beam and positive ions, which were generated in the discharge. The distance between sharp cathode and plane anode, which was made from niobium of cylindrical shape (diameter 14 mm and height 0.4 mm), was 9 mm. At such experimental conditions, the mean input power in nitrogen plasma was about 20 W.

Niobium specimens were mechanically polished with emery paper, before final polishing with diamond suspensions until their surface was like a mirror. Then they were cleaned twice in an ultrasonic bath (Elmasonic S 10H, Elma Schmidbauer GmbH, Germany) with alcohol at 50 °C. Since cleaned metal specimens are highly prone to oxidation, inert gas such as nitrogen was used for plasma treatment. After surface modification by REP DD, which was initiated in nitrogen flow rate of 5 sl/min, the changes in concentration of the main chemical elements in the surface layers were measured with Auger-electron spectrometer Shkhuna-2 (NPO "Electron", Russia). The surface free energy was evaluated by contact angle measurements performed by optical microscope (LOMO MIKMED-1 Version 2, Russia) before and immediately after plasma treatment. The surface energies, the sum of the polar energy and the dispersion energy, were calculated using the Owen-Wendt method [7] by solving the system of the OWRK equation for two different liquids with the known dispersive and polar components. During contact angle measurement, 3 µl of deionized (DI) water and glycerine were, respectively, dropped onto the metal surface at room temperature. The surface roughness of specimens before and after treatment was studied with using of a 3D contactless profilometer Micro Measure 3D Station (STIL).

## 3. Results and discussion

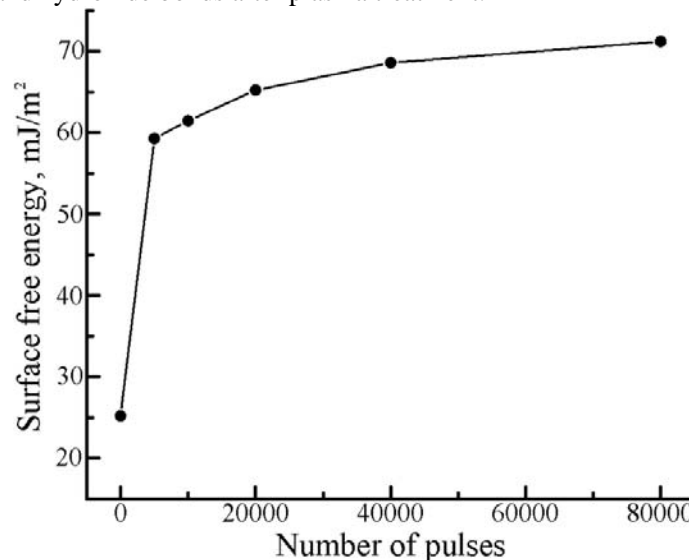
Figure 1 shows the concentration profiles of carbon (fig. 1a), oxygen (fig. 1b) and nitrogen (fig. 1c) in surface layer of niobium before and after plasma treatment with 80000 and 120000 REP DD pulses. It is seen from the figure, that carbon concentration of contaminants decreased with increasing of discharge number of pulses. The carbon concentration on the top surface after exposure by 80000 pulses decreased from 24 % at. to 20 % at. and in the underlying layer, in the depth deeper than 50 nm, it decreased 1.5 times. After plasma treatment with 120000 REP DD pulses, the carbon concentration in the whole depth decreased lower than 10 % at. Since cleaned metal specimens are highly prone to oxidation, immediately after treatment the surface has covered with thin (less than 10 nm) oxidized film, in which oxygen concentration exceeds the concentration in the untreated specimen (fig. 1b). However, after plasma treatment, in the underlying layer in the depth deeper than 10 nm, it decreased almost 2 times. Moreover, slight increasing of nitrogen concentration was found in the top surface layer after treatment by 120000 pulses (fig. 1c). It should be noted, that nitrogen concentration is below 5 % at., that is close to limit of sensibility of Auger electron spectroscopy method.

As a consequence of the cleaning, the surface free energy of the treated specimens drastically increased in the initial stage of plasma treatment and slowly increased with increasing power and number of discharge pulses. Figure 2 shows the dependence of the surface free energy versus number of discharge pulses. Before plasma treatment, surface with high content of carbon contaminants has low surface free energy value due to the weak polarity of C-C/H bonds. After removing the carbon impurity through plasma treatment, the surface free energy increases significantly.



**Figure 1.** Carbon (a), oxygen (b) and nitrogen (c) concentrations at a depth of the niobium surface before and after REP DD treatment in nitrogen flow.

As shown in figure 2, the surface free energy increased 2.8 times after treatment by 80000 discharge pulses. Moreover, the growth of the surface free energy is also due to formation of high polarity chemical groups with oxygen and hydroxide bonds after plasma treatment.



**Figure 2.** Surface free energy of niobium specimen versus number of REP DD pulses.

The surface profile measurements have shown, that plasma treatment with REP DD in nitrogen flow has polishing effect. Thus roughness parameter  $R_a$  (roughness average, nm) of the untreated niobium specimen was equal to 60 nm and after treatment with 80000 REP DD pulses it was 51.2 nm.

#### 4. Conclusion

Niobium surface treatment was performed using a nitrogen plasma of runaway electron preionized diffuse discharge generated at atmospheric pressure. From the observation of Auger electron spectra and surface free energy measurements, it is obvious that REP DD plasma treatment provides high grade of the surface cleanliness along with the intense surface free energy growth, that is important for further bonding, adhesive coating and printing.

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